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Application of bio-oils from lignocellulosic biomass to transportation, heat and power generation—A review

Soo-Young No *

Department of Biosystems Engineering, Chungbuk National University, Cheongju 361-763, Republic of Korea

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A B S T R A C T

This review will be concentrated on the application of bio-oil produced from the cellulosic biomass among the various liquid biofuels to transport fuels, heat and power generation as substitute. Main application of bio-oil and biocrude from two main thermochemical processes, i.e., pyrolysis and liquefaction include boiler for heat and electricity production, diesel engine or gas turbine for power generation, and diesel engine for transportation fuel. Fast pyrolysis is the most popular process for converting cellulosic biomass to high yield of bio-oil with relatively low cost.

For the application of bio-oils to transportation, heat and power generation, physical upgrading methods such as emulsions (bio-oil/diesel or bio-oil/biodiesel) and blends of bio-oil/oxygenated fuel (ethanol, diglyme) were mainly used and tested. The studies on the spray characteristics of emulsions and blends in diesel engine condition are not available in the literature. In most studies on the combustion and emission characteristics of emulsions and blends, CO emission was increased in most fuels and engines tested and HC was increased or comparable to diesel operation. However, NO*x* and soot emissions were decreased in most case of experiments.

In the pressure-swirl nozzle for gas turbine application, preheating and blending techniques were employed to reduce the SMD of spray. In case of blend for the application of heat and power generation, E20 blend was mainly selected in most studies. Most studies related to bio-oil combustion in burners, diesel engines and gas turbines demonstrated the higher HC, CO and soot emissions than the original design fuel.

Although the properties of bio-oil/methanol blend were widely investigated, there are no studies available about the application of bio-oil/methanol blend to transportation, heat and power generation in the literature. In addition, more research is required for the combustion of upgraded bio-oils for transportation application.

Contents

* Tel.: +82 43 261 2583; fax: +82 43 271 4413.
E-mail address: sooyoung@chungbuk.ac.kr

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1. Introduction

The depletion of fossil fuels, increasing energy consumption, and concern about green house gases emission due to global climate change had led to move towards alternative, renewable and sustainable energy sources. Biofuels are one of the important renewable and sustainable energy sources. Biofuels, particularly liquid fuels, obtained from biomasses could become a valid alternative to the use of fossil fuels in the light of the more and more stringent environmental constraints. It has been estimated by Briens et al. [1] that biomass could provide about 25% of world energy demand. The feedstocks derived from biomass that are appropriate for the production of renewable biofuels can be classified as three groups: starchy feedstocks including sugars, triglyceride feedstocks and lignocellulosic feedstocks [2–4]. In this review, the discussion will be limited to biomass based on lignocellulosic materials.

Several liquid biofuels can be produced from lignocellulosic feedstocks following two different process pathways: thermochemical and hydrolysis pathways [3] or biochemical/biotechnological and thermochemical conversion processes [5]. According to Alonso et al. [3], the thermochemical pathway includes gasification, pyrolysis and liquefaction and hydrolysis pathway includes catalytic and biochemical processes. However, Bhaskar et al. [5] classified the thermochemical conversion processes of biomass into combustion, carbonization, gasification, pyrolyis, liquefaction, co-processing (co-gasification or co-pyrolysis of biomass and coal), and hydrolysis. Excellent reviews on the thermochemical conversion of biomass such as combustion, gasification, pyrolysis and other processes can be found elsewhere [6–10]. Of these thermochemical conversion processes, lignocellulosic feedstocks can be converted into liquid fuels by three routes such as gasification, pyrolysis or liquefaction, and hydrolysis [8]. However, pyrolysis and gasification can be treated recently as the leading conversion platforms for biomass-to-liquid transportation fuels [11]. Therefore, overview of production processes and products by pyrolysis and gasification from lignocellulosic feedstocks is shown in Fig. 1. The direct use of synthesis gas (syngas) from gasification process can be treated with one of syngas utilization. However, combustion of syngas in gas engine, gas turbine and steam turbine for power generation is not included in Fig. 1. The details for the combined heat and power generation from syngas can be found elsewhere [12].

Lignocellulosic biomass, when subjected to pyrolysis processes carried out in high temperature in the absence of oxygen converts into gas, solid, and liquid products called bio-oil. Within the regime of hydrothermal processing among the thermochemical routes for biomass conversion, there are two main process groups: hydrothermal liquefaction (also known as direct liquefaction) and wet gasification. At 573–623 K and 12.2–18.2 MPa, biomass undergoes more extensive chemical reaction, yielding a hydrocarbon -rich liquid known as biocrude. Although superficially resembling bio-oil, it has lower oxygen content and is less miscible in water, making it more amenable to hydrotreating [13].

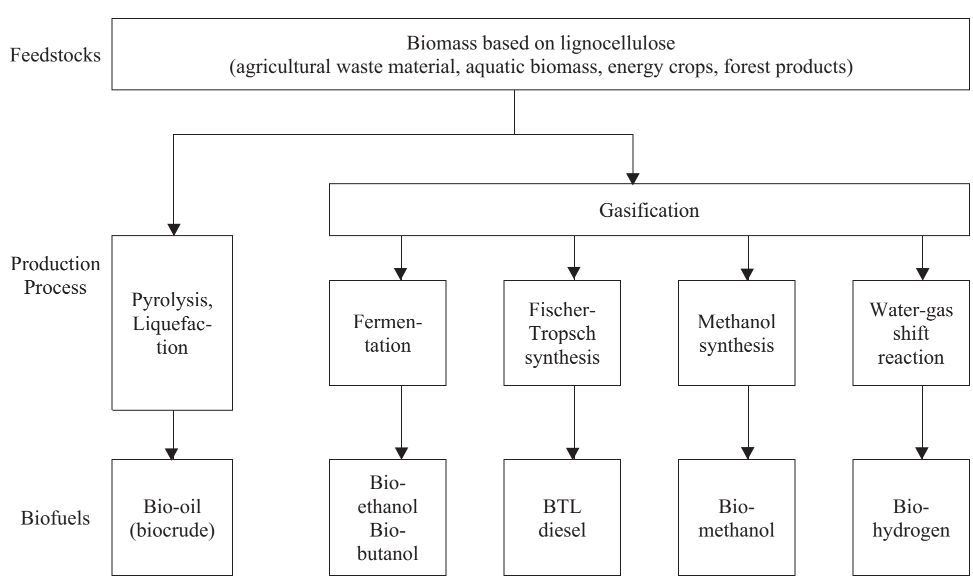

Fig. 1. Overview of production processes and biofuels from lignocellulosic feedstocks.

Of several liquid biofuels shown in Fig. 1, this review will focus on the discussion about the application of bio-oil or biocrude produced from pyrolysis or liquefaction from the cellulosic feedstocks.

The liquid pyrolytic product from the pyrolysis of lignocellulosic biomass sources is referred to in the literature by many different terms. Bio-oil [14–24] is the most widely used term in the literature. However, other terms such as bio-crude or bio crude oil (BCO) [17,25–30], bio fuel oil [17], pyrolysis oil [13,17,21,30,31–34], pyrolitic bio-oil [35], pyrolysis liquids[17,36], fast pyrolysis (bio-) oil [37–39], flash pyrolysis oil [40], biomass flash pyrolysis liquids (BFPL) [41], biomass fast pyrolysis fuel [17], biomass pyrolysis oil [19,42–44], wood pyrolysis oil [28,45], biomass pyrolysis liquid [46], fast pyrolysis liquid [17], fast pyrolysis bio-oil [47] have been used interchangeably for the liquid fuel produced by pyrolysis using biomass as the feedstock in the literature. According to the review by Mohan et al. [48] and Balat et al. [36], the synonyms for bio-oil include wood liquids, wood oil, liquid smoke, wood distillates, pyroligeneous tar, pyroligeneous acid and liquid wood in addition to the terms mentioned in the above. In this review, the term bio-oil will be used throughout the paper.

As one of the main routes for the thermal conversion of biomass into fuels and chemicals, Balat et al. [36] had extensively reviewed the pyrolysis system and bio-oils. Bio-oils have been successfully tested in furnaces, boilers, gas turbines, diesel engines and stirling engines for heat and power generation. The extensive reviews for these application were reported by Bridgwater [49], Czernick and Bridgwater [19], Oasmaa et al. [50], Mohan et al. [48], and Chiaramonti et al. [17].

For the application of bio-oil obtained from fast pyrolysis of biomass, the overview in the field of combustion of bio-oil in boilers, diesel engines, gas turbines, stirling engines for heat and power generation, as well as upgrading to potential transport fuel was reported by Czernik and Bridgwater [19], Bridgwater [49]. According to their conclusions, bio-oil has been successfully used as fuel for boiler and also showed promise in diesel engine and gas turbine applications. Upgrading bio-oil to a quality of transport liquid fuel poses several technical challenges and was not economically attractive at that time.

For the derivation of standards for bio-oil, Oasmaa et al. [50] reviewed the application of bio-oil in boilers, engines and turbines for mainly the published work in the 1990s and summarized issues related to using bio-oil as a fuel in three combustion systems. Those include high water content, solid content and viscosity as well as deposition, coking and corrosion. At the end of review for the production and the properties of bio-oil produced from mainly wood, Mohan et al. [48] briefly reviewed the bio-oil application for heat, electricity, synthesis gas and chemical production. Similarly, the progress in the application of bio-oil in power plant technologies has been reviewed by Chiaramonti et al. [17]. The main power technologies considered in this study were diesel engines, gas turbines and co-firing of biomass and coal in large-scale power stations. They concluded that bio-oil use in gas turbine plants and in co-firing mode in large power station is technically most advanced and the application in diesel engines also appears quite promising even though no long-term demonstration has been achieved. However, the application of bio-oil to transportation fuel was discussed in part or not included in those reviews. Recently, Venderbosch and Prins [51] discussed very briefly the bio-oil applications to the area of gas turbines, gasification and transportation fuels.

It is clear from the existing reviews discussed in the above that review related to the recent application of bio-oil for alternative fuel to furnaces, boilers, gas turbines and diesel engines for transportation, heat and power generation is required. The primary objective of this review is, therefore, to provide an update on the application of bio-oils produced from lignocellulosic biomass to transportation, heat and power generation. In this review, focus will particularly be concentrated on the application of bio-oil for the transportation fuel which was not discussed in the existing reviews.

2. Production of bio-oil

An excellent review for the production of bio-oil from pyrolysis of wood/biomass was reported by Mohan et al. [48]. Of several thermochemical conversion processes of biomass to biofuels, pyrolysis is defined as the chemical change occurring when heat is applied to a material in the absence of oxygen. The products of biomass pyrolysis include water, charcoal, bio-oils or tars and gases [5]. Pyrolysis can be divided into slow pyrolysis (carbonization and conventional pyrolysis), [52–54], fast pyrolysis, flash pyrolysis, ultra-rapid (ultra fast) pyrolysis, hydropyrolysis, vacuum pyrolysis and methano-pyrolysis [55]. However, the researches for producing bio-oil by vacuum flash pyrolysis [9], microwave assisted pyrolysis [56,57], and plasma pyrolysis [58] are recently reported. Of these different pyrolysis techniques, the characteristics of pyrolysis process only for bio-oil production are summarized in Table 1. Table 1 is adapted from the data of Mohan et al. [48], Demirbas [59] and Basu [55].

Of five pyrolysis processes, fast pyrolysis is now a well-established thermal processing method for converting biomass to high yield of bio-oil. Bridgwater and Peacocke [60] summarized the key feature of fast pyrolysis and the bio-oil, and described the major reaction systems and processed that have been developed over the twenty years before the year of 2000. Goyal et al. [9] reviewed mainly the pyrolysis process types and reactors, product composition and application. The product of pyrolysis depends on the design of the pyrolyzer [61], biomass type, heating rate, pyrolysis temperature and residence time in the reaction zone [55]. Akhtar and Amin [62] recently reviewed the operating parameters for optimum bio-oil yield in biomass pyrolysis. Of several operating variables such as final pyrolysis temperature, inert gas sweeping, residence times, biomass heating rate, mineral matter, biomass particle size and moisture content of biomass, they concluded that biomass type and pyrolysis temperature are two major parameters. In addition, the techno-economic analysis of bio-oil production by fast pyrolysis is available in the literature [39,63]

From the data reported by Demirbas [64], Mohan et al. [48], Huber et al. [8], Basu [55], Akhtar and Amin [62] and Demirbas [59], it can be found that temperature range of 650–905 K and pressure range of 0.1–0.5 MPa are used for fast pyrolysis. It is also found that, heating rate can be as high as 1000–10,000 °C/s.

An update on recent lab-scale research and commercial achievements in fast pyrolysis and upgrading technologies was provided by Butler et al. [65] They concluded that fast pyrolysis is a relatively mature technology and is close to commercialization stage, but upgrading of bio-oil is still in the stage of laboratory and pilot scale.

Table 1
Characteristics of pyrolysis processes for bio-oil production.

Pyrolysis process	Residence time	Heating rate	Final temperature (K)
Slow	5–30 min	Low	873
Fast	< 2 s	Very high	~773
Flash	< 1s	High	< 923
Vacuum	2–30 s	Medium	673
Hydropyrolysis	< 10 s	High	< 773

Adopted from Basu [55].

The upgrading of fast pyrolysis bio-oil is the important and main concern for many researchers involved in the area of bio-oil. The review on this title is beyond the scope of this study. The details can be found elsewhere [18,26,31,38,49,66–74]. However, it should be pointed out that recent review for catalytic upgrading of bio-oil, particularly to engine fuels have been conducted by Mortensen et al. [40]. In their review, two different main routes, i.e., hydrodeoxygenation and zeolite cracking, were proposed. In addition, an excellent updated review on upgrading of bio-oil was reported by Bridgwater [75–77].

The bio-oils can also be obtained from biomass by high pressure liquefaction. The product quality from the high pressure liquefaction is better than that from the pyrolysis. However, recent studies on bio-oils production are focused on pyrolysis because the high pressure liquefaction gives lower yield at higher cost [78]. However, pyrolysis has a lower capital cost than liquefaction.

Terms such as liquefaction bio-oil [2], liquefaction oil [8,61] and biocrude [79]are used interchangeably for the liquid fuel produced by liquefaction. According to Demirbas [79], bio-oil is the liquid fuel obtained from biomass by pyrolysis and biocrude is the liquid biofuel produced from biomass by liquefaction. In this review, the term “biocrude” will be used for the purpose of designating the bio-oil obtained from liquefaction. Typical liquefaction conditions range from 525 to 650 K of temperature, 5–20 MPa of pressure, and relatively higher temperature (650–800 K) and lower pressure (0.1–0.5 MPa) are introduced in the pyrolysis process.

According to review on process conditions for optimum bio-oil yield in liquefaction of biomass by Akhtar and Amin [80], liquefaction can be divided into two different pathways (1) pyrolytic liquefaction, where usually liquefied biomass suitably having less than 40% of moisture contents and (2) hydrothermal liequefaction, which is a solution to handle high moisture contents in biomass. Hydrothermal liquefaction [80–84] is also called hydrothermal pyrolysis [85,13], the hydrothermal process [86], hydrothermal treatment [86], and thermal liquefaction [87]. The gaseous, liquid and solid yields of hydrothermal liquefaction of biomass depend on physical and chemical parameters [88]. Of several physical parameters, range of temperature and pressure reported in the mainly review articles is summarized in Table 2. Table 2 indicates that hydrothermal liquefaction is generally carried out at 423–823 K and between 5 and 34 MPa.

The comparison of process conditions for pyrolysis and liquefaction indicates that pyrolysis occurs at lower pressure and higher temperature than liquefaction. The extensive range of production methods, upgrading and properties of bio-oil and biocrude can be found in the recent review published by Demirbas [79].

3. Properties of bio-oils and its related fuels

The physical and chemical properties of bio-oils relevant to fuel applications, under the name of biomass pyrolysis oils, were reviewed by Oasmaa and Czernik [32]. In addition, they discussed some low cost methods for improvement of fuel properties. They found that bio-oils have heating values of only 40–50% of that for petrodiesel and a high water content which is detrimental for ignition. A critical review for the physico-chemical properties of bio-oils produced from the pyrolysis of wood/biomass was reported by Mohan et al. [48]. They observed that different pyrolysis methods of biomass produce remarkably different products. The broad range of fuel properties of bio-oils is recently reviewed by Lu et al. [29]. They concluded that bio-oils are low-grade liquid fuels compared with petrodiesel and further work is required to improve the fuel properties of bio-oils.

The comparison of physico-chemical properties of bio-oils from different feedstocks showed significant difference between bio-oils [32]. The properties of bio-oils from different maker such as Georgia tech, Waterloo, SERI, Laval and VTT peat are compared by Choudhar and Phillips [61] and they found that the pyrolyzer design is one of the parameters to affect the properties of bio-oil. This is proved by Lede et al. [89] in the study of production of bio-oils with different properties in the literature by fast pyrolysis in a cyclone reactor, instead of conventional reactors.

As Huber et al. [8] pointed out, the physico-chemical properties of bio-oils obtained from fast pyrolysis and biocrude produced from liquefaction are widely different from each other. The differences in physico-chemical properties between bio-oil and biocrude produced from both processes can vary considerably due to the type of biomass feed, conditions and reactor design etc. [61]. The comparison of properties between wood-derived bio-oil and biocrude is shown in Table 3. It is clear from Table 3 that bio-oils have a higher oxygen content, moisture content, and lower heating value than biocrude.

The physico-chemical properties of bio-oil are well documented in the literature [2,17,19,76,77,91]. Therefore, in this review, the main properties related to spray and combustion characteristics for the fuel application will be discussed briefly. In addition, discussion will be divided with the physical upgrading technology or fuel optimization techniques such as emulsification and blending.

3.1. Neat bio-oil

Typical examples of physico-chemical properties of neat bio-oil from existing reviews are available from the work of Oasmaa and Czermik[32], Czermik and Bridgwater[19], Mohan et al. [48], Huber et al. [8], Chiaramonti et al. [30], Zhang et al. [43], Huber and Corma [2] and recently from Bridgwater [76,77]. It is found that the data in the works of Mohan et al. [48], Huber et al. [8], Huber and Corma [2], and Zhang et al. [43] is the same as those in the paper of Czermik and Bridgwater [19].

The comparison of properties between bio-oils from different feedstocks and diesel fuel is shown in Table 4. It is clear from Table 4 that physico-chemical properties of bio-oil is widely

Table 2
Reaction conditions of the hydrothermal liquefaction process.

Researchers	Temperature (K)	Pressure(MPa)
Demirbas [64]	525–600	5–20
Huber et al. [8]	523–598	5–20
Behrendt et al. [88]	573–773	8–24
Xiu et al. [85]	423–723	6–34
Akhtar et al. [80]	523–823	5–25
Toor et al. [83]	553–773	8–25
Karagoz et al. [86]	553	0.1

Table 3
Comparison of properties between bio-oil and biocrude.

Property	Bio-oil	Biocrude 1	Biocrude 2
Density at 55 °C (kg/m^3)	1110–1300	862–886[a]	1090–1100
Kinematic viscosity at 50 °C (mm^2/s)	10–80	23–45	2727–15596[b]
HHV(MJ/kg)	16–19	34.92–45.47	NA
Flash point (°C)	NA	63–78	NA
Moisture (%)	15–30	NA	3.5–5.0
Elemental analysis			
C (wt%)	32–49	75.9–83.4	72.6–4.8
H (wt%)	6.9–8.6	8.4–12.4	8.0
O (wt%)	44–60	3.9–15.4	16.3–16.8
N (wt%)	0–0.4	0.2–0.3	NA

Biocrude 1: Wu et al. [90] and biocrude 2: Choudhary and Phillips [61].

[a] At 30 °C.
[b] At 65 °C.

different with biomass type which is one of major parameters for bio-oil yield as pointed out by Akhtar and Amin [62]. The comparison of bio-oil from wood and agricultural residues was conducted by Oasmaa et al. [92]. Particularly, pyrolysis of sewage sludge to produce liquid for fuel use was conducted by Fonts et al. [93] and the physico-chemical properties of liquid product which is composed of three phases are reported. The top phase had a high lower heating value of 41.1 MJ/kg without water content and the lowest nitrogen and sulfur contents (2.4 and 0.2 wt%) of the three phases. This phase was miscible with diesel in the proportion top phase/diesel (1:10), indicating good properties of blending with diesel. However, the high nitrogen and sulfur contents of the middle and bottom phases make their use as a fuel oil difficult without any secondary treatment such as hydrotreating process. It should be noted that the data in Table 4 for sewage sludge is the whole sewage sludge liquid and an extensive review for sewage sludge pyrolysis for liquid production is recently reported by Fonts et al. [94].

Density of bio-oil is around 30–49% higher than that of diesel fuel. This leads to the lower calorific value because it is decreased with increase in density of fuel [95]. In addition, density of bio-oil, along with its viscosity and surface tension affects its spray and atomization characteristics in the fuel application for transportation, heat and power generation.

Viscosity of fuel plays an important role in the operation of fuel injection system in addition to the spray and atomization characteristics and subsequent combustion characteristics of fuel. The kinematic viscosity of bio-oil is much higher than that of diesel fuel, as shown in Table 4. As one of the major physico-chemical properties of bio-oil, viscosity of bio-oil from twelve different feedstocks was comprehensively studied by Nolte and Liberatore [96]. They found that the main parameters affecting viscosity were temperature and water content of bio-oils. Viscosity of bio-oil does not correlate with the acid number and pH. The linear relationship between viscosity and inverse temperature was modeled using the following Arrhenius type equation. In addition, they suggested the following power law equation for the variation of viscosity with water content.

$$\mu = A\exp(-E/RT) \quad \text{Pa s} \tag{1}$$

$$\mu = 9300\ \mathrm{WC}^{-3.8} \ \text{for} \ \ 25\ ^{\circ}\mathrm{C} \tag{2}$$

where μ is the viscosity, A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, T is the temperature, and WC is the water content.

Heating value or calorific value of bio-oil is a measure of the energy available from bio-oil when it is burned, and is the basis for calculating the thermal efficiency of a heat engine using bio-oil. The heating value of bio-oils is in the range of 13.2–32.4 MJ/kg, which is only 31–76% than that of diesel fuel (42.5 MJ/kg), as shown in Table 5. The remarkably low heating value of bio-oil compared to diesel fuel is due to high water content and oxygen content. As pointed out by Pollard et al. [97], water in bio-oil increases the amount of energy to vaporize the bio-oil, reducing

Table 4
Comparison of properties between bio-oils from different feedstocks.

Property	Pinewood	Hard wood	Soybean oil cake	Sewage sludge	Wood	Diesel
Density (kg/m^3)	1170	1232	1107 (15 °C)	1100 (20 °C)	1260 (20 °C)	820–845 (15 °C)
Viscosity (mm^2/s)	13 (40 °C)	26.5	72.38 (50 °C)	17 (20 °C)	297 (40 °C)	2–4.5 (40 °C)
LHV (MJ/kg)	18.8	14.34	33.6 (HHV)	20.9	15.27	42.5[a]
Water (wt%)	25.4	32.0	none	23.6	18.2	0.02
Solid (wt%)	0.04	< 3	–	0.12		0.01
Flash point (°C)	–	–	63			> 55
Pour point (°C)	–	–	–			N/A
pH	2.9	–	–	7.9	1.95	N/A
Elemental analysis						
C (wt%)	45.5	54.59	67.89		44.14	N/A
H (wt%)	5.8	6.74	7.77		7.0	N/A
O (wt%)	48.8	38.57	13.50		47.56	N/A
N (wt%)	< 0.1	0.1	10.84		0	N/A

Pine wood: Van de Beld et al. [101], hard wood: Tzanetakis et al. [141], soybean oil cake: Sensoz and Kaynar [16], sewage sludge: Fonts et al.[93], wood: Lopez Juste and Salva Monfort [138], and diesel: DIN EN 590: 2010-05.

[a] Heywood [153].

Table 5
Comparison of properties of bio-oil obtained by different production technology.

Property	Bio-oil [77]	Table 4 in this review	Slow pyrolysis[a]	SF bio-oil[b]	Vacuum pyrolysis[c]
Density (kg/m^3)	1200	1066–1260	1110–1100	N/A	1066
Kinematic viscosity (mm^2/s at 40 °C)	33–83	9.53–13	1.46–1.75	36–4400	38
LHV (MJ/kg)	17 (HHV)	13–20.9	N/A	18–25 (HHV)	32.4
Water (wt%)	25	18–35.5	48–56	7–15	5.3
Solid (wt%)	0.1	0.04–3.0	0.07–0.08	0.3–2.56	0.34
pH	2.5	1.95–2.9	2.95–2.98	N/A	N/A
Elemental analysis					
C (wt%)	56	44–68	N/A	51–63	77.56
H (wt%)	6	5–8	N/A	5.8–6.5	8.69
O (wt%)	38	13–49	N/A	29–41	13.13
N (wt%)	0-0.1	0–11	N/A	0.01–0.23	0.59

[a] Weerachnchai et al. [22].
[b] Fast pyrolysis of biomass as stage fractions (SF), values from SF1 to SF4 [97].
[c] Boucher et al. [100].

the net energy released during combustion. In addition, the presence of oxygenated compounds reduce the calorific value compared to hydrocarbons. According to Yaman [98], heating value of the liquids obtained from pyrolysis is nearly equal to those of oxygenated fuels such as methanol and ethanol, which are much lower than those of petroleum fuels, and the heating value of the chars is comparable with those of lignite and coke. The heating value of gases is much lower than that of natural gas, but is comparable with those of producer gas or coal gas.

Water is a major component of bio-oil, representing 5–36% by weight of the bio-oil, as shown in Table 4. Generally, even though reducing the water content of bio-oil is beneficial for the energy density(improving its heating value), stability, acidity etc., it leads to the increase in the viscosity of bio-oil [29,97,99]. This is clearly shown later in the comparison of properties of bio-oil and bio-oil derived fuels.

It is clear from Weerachanchai et al. [22] that fuel properties of bio-oil depend on the slow or fast pyrolysis and biomass resources. Three different sources such as cassava pulp residue, palm shell and palm kernel were selected to perform the slow pyrolysis in a fixed bed reactor in their study. As can be seen in Table 5, broad range of values for viscosity, density and heating were obtained according to different production technology.

It is well known that bio-oil is considered to be inferior fuel for a conventional diesel engine and upgrading is required. Even though engine modification or engine operation optimization can be introduced, fuel optimization in which fuel quality of bio-oil is improved to enable its application in diesel engines is an alternative. Recently, the physico-chemical properties of bio-oil and the different bio-oil derived fuels, i.e., upgraded bio-oils are reported by Van de Beld et al. [101] as shown in Table 6. It should be noted that for reducing the solid content in bio-oil, bio-oil is centrifuged prior to its use. It is found from Table 6 that chemically upgraded fuels such as distilled bio-oil and HPO bio-oil demonstrate higher kinematic viscosity and heating value, but lower water content than those of bio-oil and the physically upgraded fuels such emulsion and blend.

The acidity of bio-oils is typically reported by PH which is a representation of the corrosiveness of the bio-oil. However, recently the use of the total acid number (TAN) method for measuring the acidity of bio-oil was evaluated and suggested by Oasmaa et al. [102]. The concentration method was developed by Oasmaa et al. [103] for improving the storage stability of bio-oil. It can be found that both the viscosity increase-based method and the carbonyl titration method can be used for stability testing for bio-oil [104].

Table 6
Comparison of properties of bio-oil and upgraded bio-oils.

Property	Bio-oil	Emulsion	Distilled bio-oil	HDO bio-oil	Blend
Density (kg/m^3)	1170	1198	1158	1106	998
Kinematic viscosity (mm^2/s at 40 °C)	13	36	115	149	7
LHV (MJ/kg)	16.1	16.3	24.0	27.0	23.8
Water (wt%)	25.4	22.8	6.6	6.7	17.2
Solid (wt%)	0.04	–	–	–	0.02
pH	2.9	2.1	3.0	3.1	3.0
Elemental analysis					
C (wt%)	45.5	44.4	58.4	67.6	54.5
H (wt%)	5.8	6.4	7.4	8.1	8.7
O (wt%)	48.8	49.2	34.2	24.2	36.8
N (wt%)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

HDO: hydride oxygenation.
Adapted from Van de Beld et al. [101].

To summarize, it is well known that straight bio-oils are not suitable for transportation fuel due to high water content (5–36% in Table 4), high oxygen content (13–48% in Table 4) which reduce the heating value of the oil. However, by introducing stage fractions in the product recovery system, successful production of bio-oil fractions of low water content (7–15%) and decreased acidity (reduced up to 50%) is recently reported, as shown in Table 5 [97]. The main problems for operating diesel engines on neat bio-oils are inefficient ignition resulting from low heating value and high water content, corrosiveness [27] and rapid clogging of injection nozzles due to coke formed during combustion [19]. The viscosity and density of the bio-oils are considerably greater than those of the diesel fuel. This will lead to poor atomization of fuel, in turn inefficient ignition and combustion. Other main distinguished features are the high water and oxygen contents and the low heating value of bio-oils. The high water content can affect the local temperature and vaporization rate via the high heat of vaporization and specific heat. The high oxygen content will be related to the high NO*x* emission. Several physical and chemical bio-oil upgrading technologies such as blending bio-oils with organic solvents (biodiesel or oxygenates including alcohol, diglyme) and emulsification have been tested.

3.2. Bio-oil/diesel emulsion

It is well known that the physico-chemical properties of bio-oil such as heating value, cetane number, kinematic viscosity, density etc can be improved considerably by introducing the emulsion technology of mixing bio-oil with diesel as shown in Table 7. Ikura et al. [35] found that bio-oil concentration, surfactant concentration and power input per unit volume had considerable effects on emulsion stability. They also found that heating value was higher than that of neat bio-oil and viscosity of emulsion was reduced, and the corrosivity was improved compared to neat bio-oil. It is clear from Table 7 that in terms of density, HHV, viscosity, and cetane number, bio-oil concentration of less than 10% in emulsions can be acceptable as diesel fuel, especially for transport application.

To allow unmodified diesel engines to run on bio-oil without the cost and complexity of a dual fuel system, Chiaramont et al. [30] investigated the possibility of producing stable emulsions from bio-oil and diesel fuel. They reported the physico-chemical properties of three different emulsions for two different bio-oils, respectively, i.e., (1) 25% bio-oil and 74% diesel fuel, (2) 50% bio-oil and 49% diesel fuel, and (3) 75% bio-oil and 24% diesel fuel. For all emulsions, 1% surfactant was added after testing approximately 100 different surfactants. They found that the emulsions are more

Table 7
Physico-chemical properties of bio-oil/diesel emulsions.

Property	Centrifuged bio-oil	No. 2 diesel	10% Emulsion	20% Emulsion	30% Emulsion
Kinematic viscosity (mm^2/s at 40 °C)	10	1.7	3.3	4.2	6.5
Density (kg/m^3 at 20 °C)	1205	853	871	896	927
HHV (MJ/kg)	16.3	45.3	43.2	40.1	36.6
LHV (MJ/kg)	11.3	44.0	40.0	37.6	34.2
Flash point (°C)			74		62
Pour point (°C)			−24	−27	−41
Cetane number	5.6[a]	45.7	~43[b]	~38.5[b]	~34[b]

Modified from Tables 1 and 5 in Ikura et al. [35]. Emulsion with 1.5% surfactant concentration.

[a] Calculated.
[b] From Fig. 9 in Ikura et al.[35].

stable than the near bio-oil and higher the bio-oil content, higher the viscosity of the emulsion.

In addition, Xu et al. [105] had pointed out that the lubrication ability of the bio-oil/diesel emulsion was better than that of the diesel fuel, while the anti-corrosion and anti-wear properties of the fuel blend were inferior to those of diesel fuel. In this study for 10% bio-oil/diesel emulsion with 0.5 wt% surfactant concentration, the physico-chemical properties of emulsion showed the same tendency with the results obtained by Ikura et al. [35]

Recently, bio-oil blended with diesel fuel without adding any surfactant was developed by Majhi et al. [106] In their study, the physico-chemical properties of 10% IBP $<$ 140 C fraction of bio-oil blended with diesel was very similar to those of petrodiesel. They emphasized that the developed blended diesel is an eco friendly and stable fuel which can store up to 5 months.

3.3. Bio-oil/ biodiesel emulsion

As one of simple upgrading method to improve the fuel quality of bio-oil, the preparation of emulsion of bio-oil with other transportation fuels such as biodiesel is one of such trial. The fuel properties of bio-oil/biodiesel emulsion containing 10, 20, 40 and 50 mass% of bio-oils were presented by Garcia-Perez et al. [107]. They concluded that in the fuel properties of biodiesel, small increase in density and viscosity and a small change in the heating value were observed by the addition of bio-oil. However, it should be pointed out that the effect of bio-oil feedstocks on the variation of viscosity in bio-oil/biodiesel emulsion was remarkable. It should also be noted that 5 mass% of methanol was added to blends to improve thermal stability. In their continued study, the solubility of bio-oil in biodiesel was enhanced by introducing ethyl acetate as an additive [37]. In addition, the effect of bio-oils on the oxidation stability and cold flow property of biodiesel containing bio-oil fractions was conducted by Garcia-Perez et al. [21]. They found that bio-oil can be considered a good source of anti-oxidants to enhance the biodiesel oxidation stability and cold flow properties was also slightly improved. One of the undesirable result was, however, that the pH of the biodiesel was decreased. It should be noted that they had prepared the bio-oil/biodiesel blends with the addition of 5 mass% of methanol as the same as their previous study [107].

In the study on the mixture stability, Jiang and Ellis [108] suggested that the optimal conditions for producing a stable blends of bio-oil/biodiesel are with an octanol sufactant dosage of 4% by volume, 40% of bio-oil/60% of biodiesel by volume, stirring intensity of 1200 rpm, mixing time of 15 min and emulsifying temperature at 303 K. In their continued research [109], the physicochemical properties of bio-oil/biodiesel mixtures stored at different temperatures (333 and 353 K) for up to 180 h were measured. they concluded that as the change in the aged bio-oil/biodiesel emulsions was considered to be minimal, the emulsified bio-oil with biodiesel is suitable to be considered as a stable fuel during storage. However, further studies on the performance and exhaust gas emission of bio-oil/biodiesel emulsion in diesel engine will be required.

3.4. Bio-oil/ methanol blended fuel

The physico-chemical properties, stability, ageing, phase separation, and thermal shock as a fuel for gas turbine were investigated by Boucher et al. [100,110] In this study, the characterization of a vacuum pyrolysis bio-oil and the evaluation of the effect of the addition of methanol and pyrolytic aqueous phase on the bio-oil properties were conducted. The reasons for the addition of pyrolytic aqueous phase are (1) lowering the combustion temperature and thus reduce the NO_x, SO_3, and PM emission, (2) convenient way to eliminate the pyrolysis by-product, (3) providing a means of controlling the viscosity of bio-oil. In parallel to this, methanol was added to the bio-oil to improve homogeneity, facilitate its combustion and enhance its stability. Therefore, three different kinds of blends, i.e., methanol/bio-oil, aqueous phase/bio-oil, and methanol/aqueous phase/bio-oil were selected for the study. The experimental results indicated that bio-oil itself investigated in this study was a valuable liquid fuel for gas turbine in terms of Na+K+Ca content, viscosity, lower heating value, and solid content. A concentration of 10–15% of the aqueous phase in the bio-oil was optimal due to the decreasing the thermal stability and thus the phase separation at 353 K. The addition of methanol to the bio-oil was beneficial for the bio-oil properties as well as for the stability of the bio-oil and its blends. Moreover, methanol/aqueous phase/bio-oil blends delayed the phase separation process.

3.5. Bio-oil/ethanol blended fuel

The effect of alcohol addition up to 10% on the fuel properties of bio-oil was extensively examined by Oasmaa et al. [111]. Addition of methanol, ethanol, and isopropanol into bio-oil decreased linearly the viscosity, density, flash point, pour point, and increased the heating value of the blends. In addition, alcohol addition improved the homogeneity which is related to phase separation. The effect of ethanol addition up to 25% on the fuel properties of bio-oil was investigated by Moloodi et al. [112]. The addition of 25% ethanol resulted in 16% increase of higher heating value, 40% decrease of kinematic viscosity. In addition, ethanol addition improved combustion stability and reduced emissions.

Information on specifications and registration of fast pyrolysis bio-oil was provided by Oasmaa and Peacocke [113]. In this report, physical property data on a range of pyrolysis liquids from published sources have been included to provide a more comprehensive guide for users. Some new analysis method, such as solids content analysis, have been suggested in this report due to the significant difference between bio-oils and mineral oils.

During the formal pre-SIEF (Substance Information Exchange Forum) meeting on Nov. 30, 2012, the following tentative identification for REACH registration of fast pyrolysis bio-oil was obtained.

> Substance name: fast pyrolysis bio-oil
> Definition: liquid condensate recovered by thermal treatment of biomass, like wood, at short hot vapour residence time (typically less than about 10 s) typically at between 450 and 600 °C at near atmospheric pressure or below, in the absence of oxygen [114].

Although this substance identification was based on a new CAS definition (CAS RN 1207435-39-9), which was proposed by IEA Bioenergy Task 34 on March, 2010 [114,115], there are slight difference between two identifications. Instead of biomass like wood in REACH registration, lignocellulosic biomass was used in a new CAS number. In addition, vapor residence time in REACH registration was extended to about 10 s from about 5 s in a new CAS number. However, there is no explanation about the reason for extending the vapor residence time.

Oasmaa [116] provided the fuel oil specifications, test methods and testing procedures in ASTM standards and CEN standards as they are applied to bio-oil. More recently Nummisalo [117] summarized the specification for fast pyrolysis bio-oil established by ASTM and CEN standardization work, as shown in Table 8.

Standards by CEN are required to facilitate the European market penetration of fast pyrolysis bio-oils for replacing heavy fuel oil in boilers, replacing light fuel oil in boilers, replacing fuel

Table 8
Properties of fast pyrolysis bio-oils in ASTM D7544.

Property	Grade G (2010)	Grade D (2012)	Heavy fuel oil [141]
Gross heat of combustion, MJ/kg, min	15	15	40
Water content, %mass, max	30	30	<3
Pyrolysis solids content, %mass, max	2.5	0.25	1
Kinematic viscosity at 40 °C, mm^2/s max	125	125	106–1060
Density at 20 °C, kg/m^3	1.1–1.3	1.1–1.3	0.94
Sulfur content, %mass, max	0.05	0.05	–
Ash content, %mass, max	0.25	0.15	–
ph	Report	Report	–
Flash point, °C, min	45	45	–
Pour point, °C , max	−9	−9	–

oil in internal combustion engines excluding vehicle engines, suitable for gasification feedstock for production of syngas and synthetic biofuels, and suitable for mineral oil refinery co-processing. To develop quality specification of fast pyrolysis bio-oil after upgrading for the application to automotive diesel engines will be the next step.

In addition to these trials, several results of international round robin on viscosity, ageing and stability and guidelines for transportation, handling of fast pyrolysis bio-oil recently were reported by Oasmaa et al. [115] and Elliot et al. [118,119].

4. Combustion fundamentals of bio-oil

Due to the different properties such as high content of moisture of bio-oil compared to other liquid biofuel and petrodiesel, several studies on evaporation of bio-oil were undertaken. The single droplet combustion studies and full-scale combustion tests of bio-oil undertaken before 2000 s can be found in the literature review conducted by Ringer et al. [120] under the heading of combustion. They pointed out in the single droplet combustion studies that even though burn-out time for bio-oil was comparable to No. 2 diesel fuel, bio-oil demonstrated the formation and burnout of cenosphere particles and the phenomena of micro-explosion. In addition, the results of full-scale combustion tests on bio-oil conducted in flame tunnels did not show fundamental differences in combustion behavior in comparison to No. 2 diesel fuel, except the higher emissions of NO*x*, CO and PM from bio-oil.

4.1. Evaporation

Continuous thermodynamic model introduces a series of probability density functions to describe the molecular weight distribution of the components in the fuel. By using this model, Hallet and Clark [44] represented the bio-oil composition with four continuous distributions, representing the acid, aldehydes, water and pyrolytic lignin.

Hydrodynamic model was introduced by Brett et al. [24] for modeling a stationary, spherically symmetric evaporating bio-oil droplet. They assumed that the oil represented by Hallet and Clark's distribution [44] is not necessarily a good representation of many bio-oils. In this study, liquid phase diffusion was, therefore, modeled unlike in the continuous thermodynamic model. They found that the limited rate of diffusion within the droplet was shown not to affect the early stages of vaporization, but remarkably slowed vaporization later in the process.

Discrete component model based on 10 dominant components for the vaporization modeling of single bio-oil droplet was used by Zhang and Kong [23]. However, for modeling the vaporization of the mixtures of bio-oil and other practical fuels including diesel fuel, biodiesel and ethanol, they introduced the hybrid vaporization model which composed of continuous thermodynamic and discrete component approach. They found that the drop size history of single bio-oil droplet does not follow the conventional D^2-law due to its complex composition which is known as a complex fuel composed of more than 300 components [48]. Results for the fuel mixtures indicated that bio-oil droplet generally has longer lifetime than drops of other fuels and the fuel mixtures.

In the area of droplet evaporation, Sazhin [121] categorized the droplet evaporation model into empirical correlations, hydrodynamic models, multi-component droplet model and kinetic models, etc. in his comprehensive review. Multi-component drop vaporization model can be further classified as the discrete component model, the continuous thermodynamic model, and the hybrid vaporization model. It is found in this study that of these models, both the hybrid vaporization model and the kinetic model were not introduced to the researches on the modeling of the bio-oil droplet evaporation process.

4.2. Combustion

The fundamental combustion studies of bio-oil can be divided into three groups: neat bio-oil, emulsion and blended bio-oil. Overviews of these studies are provided below.

The combustion of a single bio-oil droplet was investigated by Calabria et al. [122] at similar conditions of diesel engine and by Hristov and Stamatov [123] for modeling with analytical models.

As a basic combustion study of bio-oil for the application of diesel engines, bio-oil single droplet (diameters of 400–1200 μm) with moderate and high ambient pressure (0.1–6 MPa) in a combustion chamber was suspended to a thermocouple or to a quartz fiber and were burned [122]. Several features peculiar to bio-oil droplet combustion such as swelling, vaporization, ignition and cenosphere combustion were inferred [124]. The burning of bio-oil droplets occurred in two phases: liquid (initial droplet) and solid (cenosphere) combustions. They found that bio-oil droplets were easy to ignite at normal as well as at high ambient pressure. Total burning time was decreased with decrease in droplet size up to 0.2 MPa, while showed slight increase with increase in droplet diameter for higher pressure. However, the experiment did not record the micro-explosion phenomena in this study as opposed to the result of Shaddix and Tennsion [125] and the review result of Ringer et al. [120]. A modeling study on bio-oil droplet combustion, particularly the heating period before the droplet micro-explosion, was conducted by Hristov and Stamatov [123]. The scaling and analysis of droplet combustion history showed that the diffusion limit model with a volumetric heating source and Stefan boundary condition is proper to model the initial stages of droplet combustion. They also found that explosions are impossible at low levels of the volumetric heat source.

The combustion fundamentals of droplets composed of emulsions of bio-oil in diesel fuel were investigated by Calabria et al. [126,127] A single bio-oil/diesel emulsion (bio-oil 30% in diesel fuel) droplet with the diameter of 500–1500 μm was suspended to thermocouple and was burned in a combustion chamber. It was clear that the general behavior of emulsion was intermediate between bio-oil and diesel fuel and emulsion droplet remarkably reduced the ignition time compared to the bio-oil droplet. They extended this study to the emulsion of bio-oil 10, 30% in diesel fuel with the diameter of 400–1200 μm. They concluded that the size distribution of the dispersed bio-oil droplets in the range of 3–10 μm was not effective neither for determining the overall thermal behavior nor for the effectiveness of micro-explosion.

Bio-oil and ethanol can be mixed well without using surfactant or additives and form a stable blend. A series of experiments on bio-oil/ethanol blends, i.e., 10%, 20%, and 40% bio-oil, burned in a constant volume vessel designed to simulate diesel engine condition was undertaken by Nguyen and Honery [128]. At a ambient pressure of 2.5 MPa and ambient temperature of 1100 K, introduction of up to 20% bio-oil in ethanol revealed little effect on ethanol combustion performance. Burning rate were similar for blends and ethanol. This may be due to the similar vaporization rate of blends to that of ethanol, as pointed out by Zhang and Kong [23]. They found that combustion of blends revealed the increase in combustion generated particle load, and this increased with the increase of bio-oil concentration, but remained much lower than particle concentration in diesel fuel.

5. Application of bio-oils for transportation fuel

In the classification by Zhang [129] and Nigm and Singh [130], bio-oil was not included in 2nd generation automotive alternative fuels because of several problems as an transportation fuel, such as poor volatility, high viscosity, coking, corrosiveness and high water content. In addition to bioethanol and biodiesel, which are two liquid biofuels that might replace gasoline and diesel fuel for transportation, Demirbas [79], however, recommended bio-oil as one of the competitive liquid biofuels from biomass.

Due to the inherent physico-chemical properties of bio-oil, the fuel application of bio-oils for transportation fuel is essentially related to compression-ignition (CI) or diesel engine combustion process. The essential feature of combustion in CI engine can be broadly divided into spray, combustion and emission characteristics. Overviews of these characteristics are provided below.

5.1. Spray characteristics

In the study of feasibility and perspectives of CI engines fueled by bio-oil, spray characteristics such as breakup length and spray angle by high-speed visualization for only blends of bio-oil with diglyme were reported, not for emulsion of bio-oil in diesel fuel [45]. A transparent test rig, allowing spray visualization was used to conduct tests on the behavior of bio-oil based fuels with a commercial diesel injection system equipped with a 4-holes injector. They found that bio-oil (50% in volume)–diglyme spray shows a narrower spray angle and shorter breakup length than those of diesel fuel spray. These effects may be attributed to the higher value of bio-oil viscosity than that of diesel fuel.

It is interesting that atomization quality was evaluated through the prediction of Sauter mean diameter(SMD) by the empirical correlation in the following two studies. The SMD of certain fuel spray depends on a large number of variables such as fuel properties, operating conditions, and nozzle geometry. The following empirical correlation for the SMD through dimensional analysis was suggested by Elkotb [131]

$$\mathrm{SMD} = 6156\,\Delta \mathrm{P}^{-0.54} \nu^{0.385} \sigma^{0.737} \rho_{\mathrm{f}}^{\;0.737} \rho_{\mathrm{a}}^{\;0.06} \tag{3}$$

where SMD is in μm, ΔP is the pressure drop across the nozzle (bar), ν is the kinematic viscosity of fuel (m^2/s), σ is the surface tension (N/m), ρ_f is the density of fuel (kg/m^3), and ρ_a is the density of air (kg/m^3). To examine the importance of the measured kinematic viscosity, density and surface tension differences across bio-oils and diesel fuel, Shihadeh and Hochgreb [132] had modified the above correlation and the normalized SMD with respect to diesel fuel properties suggested as follows.

$$\mathrm{SMD}/\mathrm{SMD}^{*} = (\nu/\nu *)^{0.385} (\sigma/\sigma *)^{0.737} (\rho/\rho *)^{0.737} \tag{4}$$

where ν is the kinematic viscosity, σ is the surface tension, and ρ is the density and $*$ means properties of diesel fuel at the same temperature. They assumed in the original correlation for the SMD suggested by Elkotb [131] that the pressure drop across the nozzle and air density between diesel and bio-oil are coincident, respectively. It was found that the difference in predicted SMD between two bio-oils was only 5% at 297 K and decreased with increase in temperature. In addition, the results showed that SMD of two bio-oils can arrive at the same SMD of diesel above around 473 K.

In the study of feasibility and perspectives of CI engines fueled by bio-oil, spray characteristics such as breakup length and spray angle by high-speed visualization for only blends of bio-oil with diglyme were reported, not for emulsion of bio-oil in diesel fuel [45]. They found that bio-oil (50% in volume)–diglyme spray shows a narrower spray angle and shorter breakup length than those of the diesel fuel spray. These effects may be attributed to the higher value of bio-oil viscosity than that of the diesel fuel.

The similar work with Shihadeh and Hochgreb [132] was reported by Honnery et al. [52]. It is interesting to note that experiments were undertaken to determine the performance of a direct injection CI engine fueled by blends of slow pyrolysis bio-oil known as pyroligneous tar and diesel fuel. This paper should be read with some care, however, as the correlation was poorly characterized in terms of viscosity and the different exponential value for density ratio. Instead of kinematic viscosity and exponential value of 0.737 for density ratio in the original correlation, dynamic viscosity and exponential value of 0.352 for density ratio were introduced in the correlation. They found that SMD of bio-oil was seven times bigger than that of the diesel at 293 K, but it arrives nearly same diameter with diesel at around 393 K.

It is found from this review that there is limited amount of literature data regarding the spray and atomization characteristics of bio-oil as transportation fuel for the application in CI engine.

5.2. Combustion and emission characteristics

The studies on the combustion and emission characteristics of bio-oil for transport application can be classified into the researches for neat bio-oil, emulsions and blends. Of these application methods, emulsions and blends are the included methods of physical upgrading of bio-oil to make either a transport fuel or a fuel for power generation in diesel engines [77].

5.2.1. Neat bio-oil

Two papers regarding the ignition characteristics of neat bio-oil can be found in the literature survey. Ignition delay and combustion behavior of two bio-oils produced from wood in single cylinder DI diesel engines were investigated by Shihadeh and Hochgreb [42]. While the similar thermal efficiency of around 36% can be achieved by bio-oils and diesel fuel, they also found that bio-oils showed excessive ignition delay and required a moderate degree of combustion air preheating (328 K) to ignite reliably. However, they did not report the cetane number of two bio-oils which is defined for the ignition quality of diesel fuel. In addition, they concluded from modeling results that bio-oil combustion is predominantly kinetically controlled. This is fundamentally different from the predominantly mixing controlled in diesel fuel combustion. Therefore, they suggested that the longer ignition delay observed with the bio-oils cannot be due only to poor vaporization and atomization characteristics, but is rather related to the chemical composition of the fuel.

It is known that bio-oil exhibited different ignition characteristics according to the bio-oil production process. The effect of four main pyrolysis process variables on ignition delay in CI engines was, therefore, investigated by Shihadeh and Hochgreb [132] in single cylinder, direct injection diesel engine. Four pyrolysis

production parameters include water content, extent of thermal cracking, volatiles collection temperature and the physical properties of resulting fuel. It should be pointed out that the combustion air was initially preheated up to 130 °C to allow engine operation with low cetane number bio-oil without using additives for ignition improvement. They found that water content and the extent of thermal cracking played an important role in ignition performance, with lower water content and greater cracking yielding better ignition characteristics.

5.2.2. Emulsions

To overcome the inherent disadvantages of bio-oil such as high viscosity, acidity and water content, the methods of emulsifying bio-oil with diesel fuel or biodiesel were introduced in applying bio-oil as a fuel in CI engines. A stable bio-oil/diesel or biodiesel emulsion decreases the viscosity and increased the calorific value and the cetane number as a liquid fuel [108].

For the production of low-cost and stable bio-oil/diesel emulsions, four different types of bio-oil from various feedstock and pyrolysis technology were selected and three different emulsions for two bio-oils were tested by Chiaramonti et al. [30]. They found that the viscosity and stability of emulsions are increased and improved respectively as the content of emulsifying agent is increased. In addition, the viscosity of emulsions was also increased with increase in bio-oil content. In their continued work [27], the effect of different bioemulsions (termed for bio-oil/diesel emulsions by the authors) on the injection systems of different diesel engines were investigated. They suggested that the injector and fuel pumps should be made with corrosive resistant material such as stainless steel. However, detailed analysis of engine performance and exhaust gas emissions fueled with various emulsions was not reported.

An attempt was made to apply bio-oil/diesel emulsion in a single cylinder DI diesel engine by Prakash et al. [133]. Performance and exhaust emission were measured from the engine with three different bio-oil based fuels which are bio-oil/diesel emulsion, bio-oil/diesel/2% DEE(Diethyl ether) emulsion, and bio-oil/diesel/4% DEE emulsion. The surfactant Tween 20 was used to prepare bio-oil/diesel emulsion and DEE was introduced as an ignition improver having high cetane number of more than 125. Compared to diesel fuel, the brake thermal efficiency was higher for bio-oil/diesel emulsions due to lower viscosity of emulsion and addition of ignition improver. The brake specific energy consumption was also higher in the case of emulsions because of the lower energy content. The CO emissions of bio-oil/diesel emulsions were slightly higher than diesel fuel due to poor atomization of the emulsions. The HC emissions are more in the case of emulsions due to more water content which leads to longer ignition delay and incomplete combustion. It was observed that the NO emission was lower for bio-oil/diesel emulsion due to more water content in bio-oil which reduces the combustion temperature. However, in the case of bio-oil/diesel/DEE emulsion, addition of ignition improver DEE improved the combustion which results in higher NO emissions. In the analysis of exhaust emissions, the data for PM or soot emission was not reported in this study.

Lee [134] investigated the performance and emission characteristics of DI diesel engine with common rail injection system operated with diesel, biodiesel, bio-oil/ soybean biodiesel emulsion. 4% octanol as a surfactant and 60% soybean biodiesel were mixed in the bio-oil which is the upper layer with biodiesel rich in the emulsion. Compared to diesel fuel, biodiesel and bio-oil/biodiesel emulsions showed the similar combustion characteristics based on the data of cylinder pressure, heat release rate, combustion duration, and coefficient of variance in indicated mean effective pressure. The similar fuel conversion efficiency was obtained for three fuels and it is increased up to IMEP of 0.4 MPa and then decreased linearly with increase in IMEP. Indicated specific fuel consumption for bio-oil/biodiesel emulsion was highest due to the lowest energy content in the emulsion. It was observed that the HC emissions of biodiesel and bio-oil/biodiesel emulsion were lower due to the effect of oxygen content compared to that of diesel fuel. The CO emission for three fuels showed the similar level for the engine loads considered in this study. Although NO*x* emission of bio-oil/biodiesel emulsion was nearly identical with that of biodiesel, NO*x* emission for both fuels were higher by around 5–10% due to oxygen content in emulsion compared to that of diesel fuel. It can be observed that soot emission was lowest for bio-oil/biodiesel emulsion and was highest for diesel fuel because of oxygen molecular between C–C bond.

Performance and emission characteristics of IDI diesel engine operated with diesel, biodiesel, bio-oil/diesel and bio-oil/biodiesel emulsions were investigated by Lee et al. [28]. For producing bio-oil/biodiesel emulsion, 60% soybean biodiesel and 4% octanol as a surfactant were mixed in bio-oil which is the upper layer with biodiesel-rich in the emulsion. For making bio-oil/diesel emulsion, Hypermer B246F and Hypermer 2234 as surfactants and 70% diesel were mixed in the bio-oil which is the lower layer with pyrolytic lignin-rich in the emulsion. The maximum engine torque at full load for biodiesel, bio-oil/biodiesel and bio-oil/diesel emulsions revealed the similar value due to the similar lower heating values. In the case of bio-oil/diesel emulsion, lower maximum engine torque by 10% than that of diesel was obtained. The break specific fuel consumption for four fuels considered here showed the opposite tendency with those of the maximum engine torque. The exhaust gas temperature of bio-oil/diesel emulsion revealed the lowest value due to the highest water content. The maximum cylinder pressure was nearly identical for four fuels considered in this experiment. Diesel, biodiesel, and bio-oil/biodiesel showed the typical heat release rate curve of IDI diesel engine, while bio-oil/diesel emulsion revealed the two peak values. The total unburned hydrocarbon (THC) was decreased and showed the similar value with increase in brake mean effective pressure (BMEP) for diesel, biodiesel and bio-oil/biodiesel. However, THC emission was increased after BMEP of 0.4 MPa for bio-oil/diesel. All three bio-based fuels showed the higher CO emission than diesel fuel due to the higher viscosity characteristics of bio-based fuels. In the case of NO*x* emission, biodiesel showed the highest emission and 5–10% higher emission than that of diesel because of the higher oxygen content in the fuel. Bio-oil/biodiesel emulsion showed the similar emission of NO*x* with diesel. However, bio-oil/diesel emulsion revealed the lowest emission and 30% lower emission that that of diesel due to the higher water content. The soot emission for three fuels except diesel was much lower than that of diesel due to oxygen content. In the case of bio-oil/diesel, soot emission increased abruptly beyond BMEP of 0.4 MPa. It should be noted that the experimental results for the particle number density and particle number size distribution were reported for the preparation of future emission regulations. In addition, the malfunctions reported from the operation with neat bio-oil in diesel engine [27,120] was found in the long-term application of bio-oil/diesel in this study. The deposits accumulated in the fuel supply system from bio-oil/diesel emulsion caused the output reduction because the torque was decreased by 50%.

The emulsions of bio-oil/jatropha biodiesel as fuel in single cylinder DI diesel engine were tested by Ramakrishnan et al. [135]. In their study, three different emulsions were made by taking bio-oil in 5%, 10% and 15 on a volume basis with remaining percentage of Jatropha methyl ester and Span-80 (sorbitane monooleate) as the surfactant. Compared to diesel fuel at full load, thermal efficiency was increased with increase in bio-oil content

in bio-oil/ biodiesel emulsion. HC, NO emissions and smoke opacity were decreased and CO emissions were increased as the bio-oil content was increased at full load when compared with diesel fuel. It should be pointed out that jatropha biodiesel introduced in their study is one of the leading biodiesel obtained from inedible and low cost vegetable oil [136].

5.2.3. Blends

An extensive series of experiments for four bio-oil (12.5%, 25%, 37.5% and 50% in volume basis) with diglyme blends and two emulsions of bio-oil with diesel fuel were carried out in a single cylinder DI diesel engine [33]. Diglyme was introduced into the bio-oil to improve the self-ignition characteristics. They found that bio-oil with diglyme blends, with bio-oil content up to 37.5% in volume, can be used for reliable operation of engine without any modification. Two different microemulsions with 30% (in weight) bio-oils obtained from ultra-fast and fast pyrolysis processes in diesel fuel were also successfully operated in this engine without any major troubles. In this case, the name of surfactant was not reported. In this study, the relation between ignition delay and cetane number of four bio-oil/diglyme blends revealed that ignition delay increased and in turn cetane number decreased with bio-oil concentration in blends. In addition, the cetane number of 31 was obtained for bio-oil/diesel emulsions in this study. The combustion of microemulsion with 30% bio-oil from fast pyrolysis reduced CO emissions around 43% compared with those from hydrotreated diesel fuel, while those from ultra-fast pyrolysis revealed no difference. In both bio-oils, hydrocarbon emissions were comparable to those from hydrotreated diesel fuel. There was a significant difference in NO*x* emissions for both bio-oils. NO*x* emissions from the combustion of 30% bio-oil produced by ultra-fast pyrolysis were reduced by 50% compared with that from hydrotreated diesel, whereas those produced by fast pyrolysis were increased by 22%. They reported about the problems in operation that trace of corrosion was not detected in the injection system, although residuals were occasionally found to stick on the nozzle stem and sac.

In their continued work [45], engine tests were carried out in DI diesel engine for obtaining the heat release rate, ignition delay, fuel consumption rate and exhaust emissions. They concluded that reliable engine operation was possible with a bio-oil content up to 37.5% in volume in the case of bio-oil/diglyme blends. A remarkable reduction of NO*x* and HC was identified compared to diesel fuel, while CO level was around 50% higher.

Bio-oil and ethanol can be mixed well without using surfactant or additives and form a stable blend. A series of experiments on bio-oil/ethanol blends, i.e., 10%, 20%, and 40% bio-oil, burned in a constant volume vessel designed to simulate diesel engine condition was undertaken by Nguyen and Honery [128]. At a ambient pressure of 2.5 MPa and ambient temperature of 1100 K, reliable combustion was recorded with a bio-oil content up to 20% in weight in a constant volume vessel operating at injection pressure of 18 MPa. Burning rates were similar for blends and ethanol. This may be due to the similar vaporization rate of blends to that of ethanol, as pointed out by Zhang and Kong [23]. They found that combustion of blends revealed the increase in combustion generated particle load, and this increased with the increase of bio-oil concentration, but remained much lower than particle concentration in diesel fuel.

As an another trial for the application of bio-oil/ethanol blends, performance and emission characteristics of dual injection diesel engine fueled with 60% bio-oil/40% ethanol blends were investigated by Lee et al. [137]. Pilot injection of diesel fuel at BTDC 4, 12, 20 and main injection of bio-oil/ethanol blend at BTDC 20–0 were selected in this study. For the efficient combustion of duel injection system, it was found that the optimum injection times were the pilot injection of diesel fuel at BTDC 12–20 and main injection of bio-oil/ethanol blend at BTDC 12–0, respectively. The fuel conversion efficiency of dual injection was lower by 5% than that of single injection of diesel fuel due to the lower injection pressure, water content in bio-oil. Compared to the single injection of diesel fuel, NO*x* emission and soot can be decreased by 60% and 75% respectively for dual injection system due to the water content in bio-oil.

Bio-oil obtained from slow pyrolysis can be mixed well with diesel fuel without using surfactant or additives to form a stable blend. While the slow pyrolysis is used to produce mainly charcoal and gas, examinations of the potential for the pyroligneous tar(PT) produced from by-product liquid of slow pyrolysis to fuel diesel engines were reported [52,54]. PT produced by distillation from corncob tar, designated burning oil of biomass(BOB) in the original paper, has the potential to fuel diesel engines [54]. According to the distilling temperature of biomass corncob tar, two different PTs, i.e., BOB1 and BOB2 were extracted respectively. Two blends were derived by blending 10% BOB1 and 10% BOB2 with diesel fuel by volume, respectively. The fuel properties are shown in Table 9. They found that there is no remarkable difference in performance between diesel fuel and blends. They emphasized that fuel consumption rate and CO_2 emission for PTs were much lower than those of the diesel fuel.

Experimental study for the performance of a four cylinder, direct injection, compression ignition engine fueled by blends of kiln-produced pyrolygneous tar (PT) and diesel was undertaken by Honnery et al. [52] for blends containing 20% and 40% PT with diesel. As can be seen in Table 9, the kinematic viscosity of PT is higher around 110 times than that of diesel. At fuel injection temperature over 393 K, the viscosity of PT is likely to be lower than diesel. They assumed that the viscosity effect will be negligible due to the fuel temperature at the nozzle exit will likely be well above 373 K [132]. The results indicated that addition of 20% PT by weight to diesel revealed little difference in performance relative to diesel fuel. The operation for the case of the blend containing 40% PT is required to optimize the injection timing or to preheat the air. As pointed out as a future work by the authors, exhaust emission characteristics of the blends are required.

It is clear from this review that one of the physical upgrading methods for reducing the viscosity and improving the stability of bio-oils is the solvent addition in bio-oil. Two oxygenated fuels, i.e., diglyme and ethanol were used as the solvents in the application of bio-oil blends for transportation. However, Garcia-Perez et al. [107] pointed out that the economic feasibility of these physical upgrading methods, i.e., emulsion and blends is limited by the high cost of cetane improvers, solvents and emulsifiers.

Table 9
Fuel properties of different pyroligneous tar.

Property	PT	BOB1	BOB2	Diesel
Density(kg/m^3) at 20 °C	1031	1006	1010	852
Kinematic viscosity (mm^2/s) at 20 °C	706	9.1	14.82	6.45
Flash point (°C)	49	94	108	60–70
LHV (MJ/kg)	35.6	36.4	37.1	43.5
Elemental analysis				
C (wt%)	80.0	73.7	76.3	86.0
H (wt%)	9.7	11.4	11.67	13.6
O (wt%)	10.3	10.0	10.1	0
N (wt%)	<0.05	–	–	<0.05
S (wt%)	–	–	–	–
Water (wt%)	1.22	–	–	<0.02

PT: pyroligneous tar, Honnery et al. [52] and BOB1 and BOB2: burning of biomass, Zhang and Wang [54].

6. Application of bio-oils for heat and power generation

Bio-oil can be a substitute for fuel oil or diesel fuel in many stationary applications including boilers, furnaces for heat generation and diesel engines, gas turbines for electricity generation. Several previous studies have investigated the potential for applying bio-oil in small to large scale heat and power generation systems. The essential feature of combustion in these applications can be broadly divided into spray, combustion and emission characteristics. Overviews of these characteristics are provided below.

6.1. Spray characteristics

The literature review shows several studies on spray characteristics of neat bio-oil and bio-oil/ethanol blend for gas turbine applications and bio-oil/diesel emulsion for boilers.

As a preliminary test on combustion of neat bio-oil in a gas turbine combustor for power generation, spray characteristics of bio-oil/ethanol blend were studied by Lopez Juste and Salva Monfort [138]. To obtain the similar viscosities to those of the standard fuels used in gas turbines in the typical ranges of temperature, i.e., lower than 10 mm^2/s, they measured the variation of kinematic viscosities for neat bio-oil and several bio-oil/ethanol mixtures with temperature and then selected E20 (bio-oil/20% ethanol blend) blend with the preheating temperature of 80 °C. The smaller spray angle was obtained for bio-oil/ethanol blend compared to that of JP-4. Although three different empirical correlations for the prediction of SMD was introduced in this study, no experimental data or comparison of it with the correlations were reported.

Garcia-Perez et al. [139] had studied the spray characteristics of neat bio-oil with preheating (293, 343, and 353 K) from two commercial pressure-swirl nozzles. It should be noted that bio-oil investigated in this study was produced from vacuum pyrolysis of softwood bark. Flow characteristics in terms of flow number and drop size distribution in terms of Rosin–Rammler empirical distribution function and SMD were analyzed. They found that due to the higher viscosity, the higher SMD was obtained for bio-oil sprays compared with that of heating oil and water considered here for comparison. They concluded that bio-oil with atomizer considered here can be applied to the industrial gas turbine because it was possible to obtain sprays with SMD values lower than 50 μm.

Among the various spray characteristics of bio-oil/diesel emulsion, Chiaramonti et al. [140] have measured SMD (Sauter mean diameter) of B10 emulsion (10% bio-oil/90% diesel emulsion) for the application to boiler with the variation of injection pressure and proposed the following correlation for the prediction of SMD of bio-oil emulsion sprays.

$$\mathrm{SMD} = 599.2\ \mathrm{FN}^{-0.393}\Delta P^{-0.418}\nu^{0.251}\sigma^{0.277} \tag{5}$$

where FN is the flow number, ΔP is the pressure drop in the nozzle, ν is the kinematic viscosity of fuel, and σ is the surface tension of fuel. They assumed that flow number, injection pressure, kinematic viscosity and surface tension of fuel considered play important role in fuel atomization. Even though they mentioned the correlation suggested by Wang and Lefebvre for the comparison, this correlation was not clearly explained in the manuscript, even in the references. They found that in order to obtain the same size of droplet with diesel fuel, a slight increase of injection pressure is necessary for B10 emulsion. In addition, they suggested that as an alternative, a slight preheating of emulsion leads to the reduction of viscosity of fuel, in turn, to the reduction of SMD. However, further experiment for the different emulsions and validation of the proposed correlation is required.

In order to quantify the relative difference in spray quality between bio-oil and heavy fuel oil (No.6) in the boiler application, SMD was predicted by taking the ratio of Ohnesorge numbers between bio-oil and heavy fuel oil [141]. The result for the ratio of SMD between the two fuels based on liquid density, viscosity, and surface tension indicated that bio-oil must produce a spray which has a SMD 76% lower than heavy fuel oil. However, the effect of air-to-liquid mass flow rate ratio, one of important parameter for air-assist or air-blast atomizer, was not taken into account. In addition, correlation for the prediction of SMD was not clearly illustrated in this work.

In their continued study [142], the following correlation for the prediction of SMD was selected [143].

$$\mathrm{SMD} = 0.95\left[\frac{(\sigma m_L)^{0.33}}{\rho_L^{0.37}\rho_A^{0.37}U_R}\right]\left(1+\frac{1}{\mathrm{ALR}}\right)^{1.70} + 0.13\left(\frac{\mu_L^2 d_0}{\sigma\rho_L}\right)^{0.5}\left(1+\frac{1}{\mathrm{ALR}}\right)^{1.70} \tag{6}$$

where d_0 is the nozzle diameter, σ is the surface tension of liquid, ρ_A and ρ_L are the air and liquid densities, respectively, U_R is the relative velocity between the air and liquid, and ALR is the air/liquid mass ratio. They used the above correlation in order to get the effect of atomizing air flow rate on the droplet size distribution. They found that SMD decreases appreciably with increase in atomizing air flow rate.

To compare the atomization quality between the various test run in internal-mixing air-blast nozzle for the boiler application, however, the same research group [112] selected the following different empirical correlation for the same size burner with the above correlation [143].

$$\frac{\mathrm{SMD}}{d_0} = 0.48\left(\frac{\sigma}{\rho_A U_R^2 d_0}\right)^{0.4}\left(1+\frac{1}{\mathrm{ALR}}\right)^{0.4} + 0.15\left(\frac{\mu_L^2}{\sigma\rho_L d_0}\right)^{0.5}\left(1+\frac{1}{\mathrm{ALR}}\right) \tag{7}$$

It should be noted that the dominating parameters for SMD in air-blast atomizer such as Weber number, Ohnesorge number, and air-to-liquid mass flow rate ratio are all included in this empirical correlation. As a simple upgrading method for improving the fuel properties of bio-oil, bio-oils mixed with 5%, 10%, 15%, 20%, and 25% volumetric ethanol were also tested in this study (E5, E10, E15, E20 and E25 hereafter). Based on their SMD prediction, it is easily found that SMD is decreased from 23.6% for E5 to 30% for E25 compared to E0 (neat bio-oil). It is, therefore, easy to identify the addition of ethanol to bio-oil reducing the SMD predicted by the above correlation due to the decrease of kinematic viscosity with increase in ethanol content.

Recently, Gullberg and Marklund [144] conducted the experimental study on the spray characteristics of neat bio-oil in externally gas-assisted atomizer for the gasification of bio-oil which is one of upgrading methods of bio-oil. Three different parameters i.e. ambient pressure of 0.1, 0.3 and 0.5 MPa, bio-oil preheating temperature of 295, 306, and 315 K, and the length of external extension of the prefilming center bluff body in the nozzle of 0 and 3 mm were selected in this study. They found that SMD was increased when the ambient pressure and length of central bluff body were increased. In addition, SMD was decreased with increase in the preheating temperature of bio-oil, but should be moderate due to possible polymerization of bio-oil at higher temperature more than 323 K.

6.2. Combustion and emission characteristics

Most studies on combustion and emission characteristics of bio-oil for heat and power generation have evolved from tests at atmospheric pressure in combustion tunnels and boilers to high-pressure tests in gas turbine and diesel engines.

6.2.1. Gas turbine

The researches on burning bio-oils in gas turbine before year of 2000 are available in the literature review performed by Boucher et al. [100]. To supply the background information on bio-oils regarding their application for gas turbine, they had selected the bio-oil obtained by vacuum pyrolysis of softwood bark residues and investigated the several fuel properties such as density, viscosity, surface tension, heating value including elemental analysis. They concluded that bio-oil sample investigated in their study is a valuable liquid fuel for gas turbines, even though the bio-oil requires minor improvement. They recommended that the mixtures of bio-oil with methanol or aqueous phase will be a good solution for improving some properties of the bio-oil.

The combustion of bio-oil and bio-oil/ethanol mixtures and their possible use in a gas turbine combustor without modifications was evaluated by Lopez Juste and Salva Monfort [138]. They found that for some operation conditions, the combustion performance of the 80% bio-oil/20% ethanol blend was similar to that with JP-4, being obtained with comparable values of temperature rise, combustion efficiency and CO and NO*x* emissions. However, the range of efficient operation of the combustor in terms of equivalence ratio and load parameter generally decreases compared with the operation with JP-4. They also reported the indication of a bigger tendency of bio-oil/ethanol blend to generate acoustic instabilities of low frequency.

Emission characteristics from diesel, biodiesel, bio-oil/diesel emulsion, biodiesel/diesel emulsions were measured in a swirl-stabilized burner replicating typical features of a gas turbine combustor [145]. The bio-oil/diesel emulsion was formulated by mixing diesel of 45%, bio-oil of 15% and surfactants of 40% by volume. It should be pointed out that they did not introduce the popular and commercial surfactant. The surfactants for producing emulsion were a blend of biodiesel of 30%, 2-ethyl-1-hexanol (an alcohol) of 8% and n-octylamine of 2%. Effects of atomizing air and fuel on NO*x* and CO emissions were analyzed. Results revealed that NO*x* and CO emissions are lowest for biodiesel with 25% atomizing air. For bio-oil/diesel emulsion, CO emissions were relatively low, but NO*x* emission were highest due to the nitrogen-containing surfactants in the fuel. They suggested that NOx emissions from bio-oil/diesel emulsion flame could be decreased remarkably by choosing an alternative to the nitrogen-containing surfactant to eliminate the fuel-bound nitrogen. However, it should be considered that the surfactant concentration in the emulsion is rather too high in formulating the emulsion.

Bio-oil was tested in a small commercial gas turbine with a rated electric power output of 75 kW [146]. The tests have shown that bio-oil as a substitute can successfully burn in a gas turbine together with diesel fuel in dual-fuel mode in two separate nozzles. However, it was found that an improvement in oil quality, the adjustment of the combustor and fuel supply system are required in order to achieve the optimum results. When the know-how on burning bio-oil in small or micro gas turbine engine is matured, it will be possible to extend this technology to hybrid micro-gas turbine power system (65 kW) for automotive applications [147].

6.2.2. Boiler

The flue gas emissions and ash deposition resulting from fast pyrolysis bio-oil combustion in 100 kW pilot-scale combustion test rig was investigated by Khodier et al. [148] The preheating of neat bio-oil and burner with air-assist nozzle was used in this experiment. They found that major source of NOx in flue gas is from the fuel bound nitrogen, i.e., fuel NO, not thermal NO. In addition, high combustion efficiency and relatively low ash deposition rates were obtained during combustion of bio-oil. They concluded that the deposit formed has a low corrosion potential.

The application of fast pyrolysis bio-oil obtained from rice husk to boiler was recently investigated by Zheng and Kong [47]. In their study, internal mixing air-blast atomizer was introduced and they concluded that this nozzle can obtain a find atomization because the amount of the droplet whose size is less than 50 μm was 80% and the mean droplet size was 39.5 μm. However they did not explain the measurement location exactly and the kind of mean diameter [143]. They have also measured the exhaust gas emissions such as CO, NO*x*, SO*x* and O_2 with the variation of equivalence ratio. The operation of combustor was successful after 40 min of start-up and the temperature in the center of combustor was around 1700 K for the operation of fuel rich mode. They found that with increase in equivalence ratio, CO emission was decreased, but NO*x* and O_2 emissions were increased. Negligible amount of SO emissions was measured.

Systematic research on the production, handling, and application of bio-oil under the consortium of four companies in Finland has been carried out and reported by Solantausta et al. [149] Bio-oil had been produced from sawdust and forest residues by using a bubbling fluidized-bed pyrolysis reactor. In this project, around 40 tons of bio-oil had been burned in 1.5 MW district heating plant with high efficiency. Their experimental results revealed that flue gas emissions such as CO, NO*x*, PM and organic compounds as well as no odor emission were close to those of heavy fuel oil.

For the application of bio-oil to furnaces, kilns and boilers, combustion characteristics of bio-oil and bio-oil/ethanol blend was investigated by Stamatov et al. [53]. It should be noted that they concentrated on bio-oil produced from slow pyrolysis, not fast pyrolysis, because it is potentially valuable bi-product of Australian charcoal industry. Samples of neat bio-oil, ethanol, E20 blend, E80 blend(by weight) burned in a circular jet spray combustor at atmospheric pressure. They found that bio-oil flames are shorter, wider and brighter than diesel fuel flames at the same conditions. However, this is controversial because Tzanetakis et al. [150] summarized from the literature before year of 2000 that flame length of bio-oil have a similar or longer flame length compared to petroleum oils. In the case of blends with ethanol, some of the undesired properties of the fuel such as increased viscosity, low calorific value, poor atomization and high NOx emission from the flame could be improved. However, adding of ethanol leaded to a reduction of heat flux from the flame.

To better understand the combustion and emission behavior in stationary heat and power applications of bio-oil, a series of works on combustion and emission characteristics of bio-oil/ethanol blend were reported by Tzanetakis et al. [142,150,151] and Moloodi et al. [112]. Initially, spray combustion and gaseous emission characteristics of bio-oil/ethanol blend in a pilot stabilized swirl burner were investigated [142]. The bio-oil blended with 20% ethanol by volume (E20)was chosen to increase the overall volatility of the fuel and promote flame stability. The flow rate for 10 kW operation of swirl burner equipped with internal mixing, air-blast nozzle was constructed for understanding the effect of displacing existing fuel oil with bio-oil in intermediate-size boilers. They concluded that it is essential to have thorough mixing, internal recirculation and good atomization of fuel to promote the burnout of nonvolatile material and decrease CO and HC emissions. It was also confirmed that NO*x* emissions from these flames is dominated by the conversion of fuel-bound nitrogen [148].

Further study on spray combustion and PM emission of a E20 blend in the same swirl burner with the previous study were extensively analyzed by Tzanetakis et al. [151]. The effects of swirl number, atomization air flow, pilot energy, air/fuel preheat and equivalence ratio on burn out and PM emissions were

investigated. They found that either a reduction in swirl number or low atomizing air flow leads to the increase in PM and HC emissions compared to baseline burner operation. However, the pilot flame energy, primary air and fuel preheating temperature and equivalence ratio revealed no apparent effect on PM emission. They concluded that increase in the residence time of droplets in the hot combustion zone by increasing swirl number or decrease in the mean diameter of droplet in the spray by increasing atomizing air flow rate both promotes the burnout of solid residues.

Comparison of combustion and emission characteristics of bio-oil/ethanol blend with No. 2 and No. 4 fuel oils in the same swirl burner with the same nozzle was conducted [150]. It should be pointed out that all fuels reach a similar viscosity in the nozzle by introducing preheating technique and that viscosity does not play an important role in determining the relative atomization quality between the fuels. Of two distinct batches of bio-oil, batch 1 was used to make gaseous pollutant emission measurements and batch 2 was used to measure PM emissions. Bio-oil/ethanol blend had the highest HC and CO emissions primarily because of poor atomization quality and overall volatility compared to the fuel oils. The NO*x* emissions for bio-oil/ethanol and No. 4 fuel oil were higher than No. 2 fuel oil due to their inherent nitrogen content. The No. 4 fuel oil was highest, and bio-oil/ethanol blend was higher PM emissions than that of No. 2 fuel oil because of their ash content and nondistillable residual fractions. Carbon burnout analysis revealed that bio-oil/ethanol blend has a lower combustion efficiency than both No. 2 and No. 4 fuel oils. They pointed out that the most common practical problems encountered during bio-oil combustion in boilers and furnaces include poor ignition, fuel nozzle clogging, and corrosion of mild steel components.

In their continued work of fuel property effects on combustion and emission characteristics [112], they found that CO and unburned HC decrease with both higher water and ethanol contents. In addition, increasing the volatile content of bio-oil by blending in ethanol was shown to improve flame stability due to the variation of ignition characteristics. Based on the test of E5, E10,E15, E20, and E25, they recommended that E10 blend is suitable for combustion stability in small scale bio-oil burner

6.2.3. *Diesel engine for power generation*

Assessment of the technical and economic performance of thermochemical conversion processes of biomass to electricity generation from a wood chip feedstock by combustion, gasification and fast pyrolysis was undertaken by Bridgwater et al. [152]. They concluded that fast pyrolysis and diesel engine system has great potential to generate electricity at a profit in the long term, and at a lower cost than any other electricity generation system. It should be noted that dual fuel engine with diesel as pilot fuel and with bio-oil as main fuel was selected for the analysis.

The experimental study of emulsification of the aqueous bio-oil fraction with petrodiesel under ultrasonic conditions and the combustion characteristics of the emulsion in diesel generator was recently conducted by Li et al. [46]. In this study, four surfactants such as Span 80, Tween 80, Tween 20 and n-octanol was introduced. Compared to petrodiesel, CO_2 emission increased 13.3% and CO and SO_2 emissions increased sharply to five times and twenty times, respectively, while NO*x* emission decreased around 87%. It should be pointed out that corrosion and blockage caused by coking of the injector was obvious.

The effect of the various parameters on engine performance has been investigated using a one-cylinder, 20 kW diesel engine for power generation which is installed a corrosion resistant fuel pump and injector to enable the feeding of five different fuels including neat bio-oil and four upgraded bio-oils [101]. Parameters in this experiment include the electrical load, compression ratio, addition of cetane number improver(BERAID 3450), ignition timing, air preheating temperature and type of fuel. The cetane number of 20–25 was estimated in this study. However, it should be pointed out that based on summary by Oasmaa and Peacocke [113], values of 5–6 or around 10 for bio-oil were reported. The all bio-oils used in this study was centrifuged prior to its use. First upgraded bio-oil, referred to as “Mild-HDO”, was the product from the mild hydrodeoxygenation treatment. Second one, referred to as “PO-Ester”, was the products from a reactive distillation process with butanol. Emulsion with 95% of bio-oil, 5% biodiesel and a small amount of Athlox emulsifier was introduced as third fuel. The blend used in the engine tests consisted of 60 wt% bio-oil, 30 wt% butanol and 10 wt% biodiesel. To the best knowledge of the author, this study is the first application work for the upgraded bio-oils. The neat bio-oil could be successfully used as a fuel provided the air inlet temperature was around 40 °C and 100–120 °C at an engine compression ratio of 22.4 and 17.6, respectively. The application of neat bio-oil in this study leaded to higher CO emissions and lower NO*x* emissions compared to the diesel, biodiesel and vegetable oils. Generally, compared to neat bio-oil, the four upgraded bio-oils were easier to burn resulting in lower CO emissions and higher NO*x* emissions, whereas the effect on overall efficiency was less pronounced. However, a modified fuel supply system was required in all cases due to acidity of all fuels considered. A binary blend of ethanol and bio-oil without any cetane number improver has been tested in more detail. 30 wt% addition of ethanol to bio-oil revealed the improvement in the overall engine performance with respect to overall electrical efficiency. However, significant decrease in CO and increase in NO*x* emissions was observed.

As pointed out by Moloodi et al. [112], more studies about the technical challenges associated with the bio-oil application for heat and power generation such as poor ignition quality, rapid injector clogging from solids and polymerized material, significant residue formation and coke deposition with the combustion chamber, and hot alkali corrosion from ash in the fuel are required.

7. Discussions and summary

The main applications of bio-oil and biocrude from two main thermochemical processes, i.e., pyrolysis and liquefaction, available for converting lignocellulosic biomass into useful energy form can be summarized in Fig.2. The term “biocrude” is suggested in this study for the purpose of designating the bio-oil obtained from liquefaction. Bio-oils must be upgraded if they are to be applied as transportation fuels. Bio-oils can be used as diesel engine and gas turbine fuels for power generation, and as boiler fuel for heat production. In addition, chemicals can be obtained from bio-oil by extraction or reaction. It should be noted that gasification and co-firing of bio-oil was included in the application of bio-oil by Balat et al. [36]. However, gasification of bio-oil is recently classified into one of upgrading technology of bio-oil by Butler et al. [65]. In this review, the application of bio-oil or biocrude to the production of chemicals was beyond the scope of this study.

Of several pyrolysis processes, fast pyrolysis is the general thermal conversion process for converting lignocellulosic biomass to high yield of bio-oil with relatively low cost. Even though the physico-chemical properties of biocrude are much better than those of bio-oil for fuel application, yield of biocrude is lower at higher cost than that of bio-oil. The research for the application of biocrude to transportation, heat and power generation is, therefore, not available in the literature.

The properties of bio-oil vary significantly depending on the feedstock, the pyrolysis process, reaction parameters and the

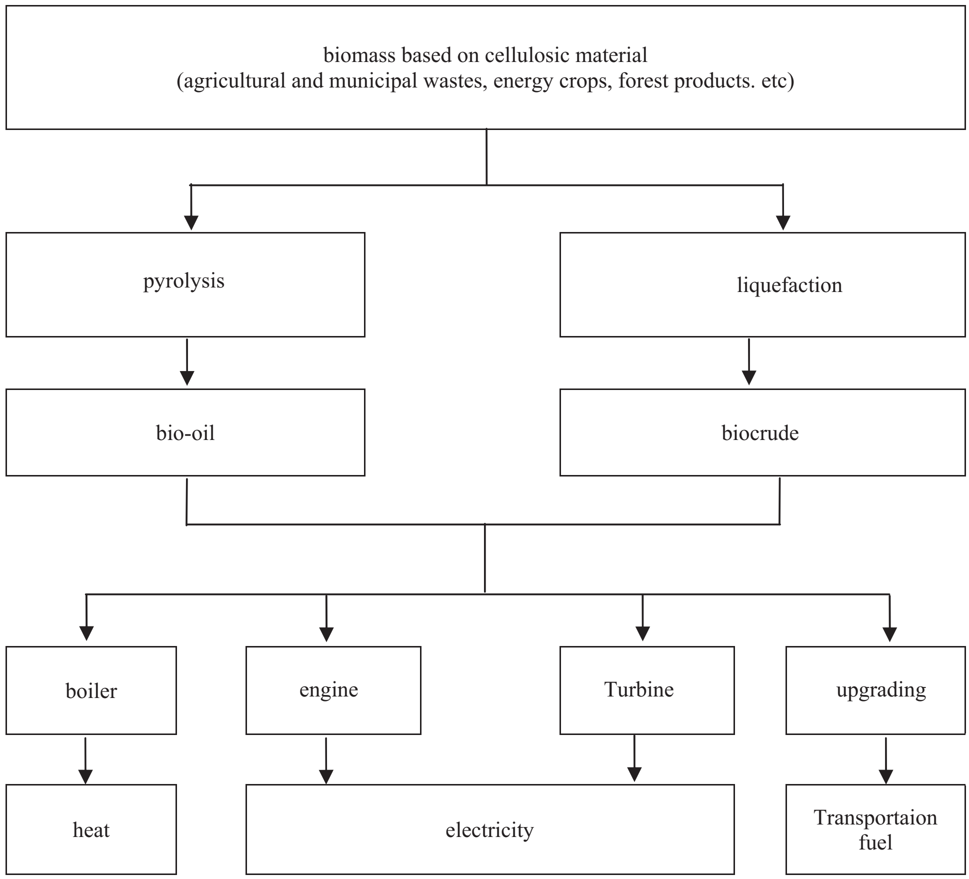

Fig. 2. Overview of production process and application of bio-oil and biocrude.

product recovery system. It is clear that neat bio-oils obtained from fast pyrolysis are not suitable for transport fuel, even for the application of heat and power generation. Several physical, chemical and catalytical upgrading methods are developed. For the application of bio-oils to transportation, heat and power generation, the physical upgrading method was only introduced. Of several physical upgrading methods, emulsions and solvent addition (blending) were mainly used. These methods can be treated with fuel optimization. In addition, bio-oil could be upgraded by process optimization of fast pyrolysis such as the introduction of stage fractions in the product recovery system. To summarize, both process optimization (pre upgrading method) and fuel optimization (post upgrading method) should be more investigated in the future.

In the single droplet combustion studies of bio-oil, although burn-out time for bio-oil was comparable to diesel fuel, bio-oil revealed the different features compared to diesel fuel combustion such as swelling, vaporization, ignition and formation and burnout of cenosphere particles, and the phenomena of microexplosion, especially in case of bio-oil emulsion.

The studies on the spray characteristics of bio-oil/diesel emulsion, bio-oil/biodiesel emulsion, bio-oil/oxygenated fuel blend in diesel engine conditions for the application of transportation are required. Many studies on the combustion and emission characteristics of bio-oil/diesel emulsion, bio-oil/biodiesel emulsion, and bio-oil/oxygenated fuel blends in DI, IDI and dual fuel diesel engines were undertaken. Compared to diesel operation, CO emission was increased in most fuels and engines tested and HC was increased or comparable. However, NO*x* and soot emission were decreased in most studies. The drawbacks of bio-oil/diesel emulsion in engine applications are corrosion/erosion, cost of surfactants, and the high energy required for emulsification. However, studies related on these technical challenges were not available in the literature.

Even though bio-oil blended with diesel without adding any surfactant is developed, in most studies for producing bio-oil/diesel emulsion, Tween 20, blend of biodiesel, alcohol, and n-octylamine, blend of Hypermer B246F and Hypermer 2234 and blend of Span 80, Tween 80, Tween 20 and n-octanol are used as surfactant. In addition, Span 80 and Octanol were applied to the production of bio-oil/biodiesel emulsion as surfactant. Small amount of DEE (Diethyl ether) or diglyme were introduced to bio-oil as ignition improver respectively. As blend of 5–7 vol% biodiesel and 95 vol% petrodiesel is currently widely used in the European transportation market, the test of a blend of 5–7 vol% bio-oil and 95 vol% petrodiesel in automotive diesel engine is required.

Several studies on spray characteristics of neat bio-oil and bio-oil/ethanol blend for gas turbine application and bio-oil/diesel emulsion for boilers were reported. In the pressure-swirl nozzle for gas turbine application, SMD can be decreased by employing both the preheating and/or the addition of ethanol to neat bio-oil due to the reduction of kinematic viscosity of bio-oil.

In the combustion studies for heat and power generation, bio-oil/ethanol blends, and bio-oil/diesel emulsions were tested in gas turbine, and neat bio-oil, neat bio-oil with preheating, and bio-oil/ethanol blend were examined in boiler and furnace application. The ethanol addition to bio-oil improved combustion stability and homogeneity, decreased the viscosity and density, lowered the flash point, increased the heating value and reduced emissions. In case of bio-oil/ethanol blend, the bio-oil blended with 20% ethanol by volume was mainly selected in most studies.

Several researches have confirmed that NO*x* emissions from bio-oil combustion are mainly originated from the conversion of fuel bound N_2.Most studies related to bio-oil combustion in small

scale burners and large scale stationary diesel engine or gas turbines showed higher HC, CO, and particulate matter (soot) emissions than the original design fuel.

Although the properties of bio-oil/methanol blend was investigated, there are no studies available about the application of bio-oil/methanol blend to transportation, heat and power generation in the literature. In addition, more research is required for the combustion of upgraded bio-oils for transportation application. The research on hybrid vehicle equipped with bio-oil fueled micro-gas turbine can be one of further study because bio-oil should be upgraded for the automotive application.

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